of basic aluminum oxide (activity I, Merck). After 6 hours' stirring at room temperature the aluminum oxide is filtered off and extracted several times with chloroform. After removal of the solvents the isomeric mixture *(7b)* is obtained quantitatively as a yellow oil, which can be separated by chromatography on silica gel [^{1}H-NMR (C_6D_6): $\delta = 6.09$ for the one isomer and 6.83 for the other (t, $J = 7$ Hz; d, $J = 3$ Hz; 4H)], though this is not necessary for the next step, *i.e.* for the synthesis of *(8b)*.

Synthesis of *(8b)*: A solution of cerium(IV) ammonium nitrate (9.0 g) in acetone (120 ml) is added dropwise (*ca.* 1 h) to a solution of *(7b)* (1.0 g) in acetone (50 ml) at 0 °C. The mixture is stirred for 0.5 h, treated with 200 g of ice and extracted twice with ether. The extracts are evaporated down and the residue taken up in ether again, washed with water and dried over $MgSO_4$. After removal of solvent the residue is dissolved in hexane and filtered through a small amount of Florisil: yield 0.42 g (95%) pure *(8b)*.

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CAS Registry numbers:
(5a), 4341-76-8; *(5b)*, 111-12-6; *(5c)*, 1846-69-1; *(5d)*, 10564-83-7; *(6a)*, 71250-41-4; *(6b)*, 71276-88-5; *(6c)*, 71250-40-3; *(6d)*, 71250-39-0; *(7a)*, 71250-38-9; *(7b)*, 71250-37-8; *(7c)*, 71250-36-7; *(7d)*, 71250-35-6; *(8a)*, 14369-81-4; *(8b)*, 71277-73-1; *(8c)*, 71250-11-8; *(8d)*, 71250-12-9; *(9)*, 50320-90-6; *n*-$C_9H_{19}C{\equiv}C{-}CHO$, 71250-13-0; MnL_3(*n*-$C_9H_{19}C{\equiv}C{-}CHO$), 71250-34-5; MnL_3(*n*-$C_8H_{17}CH{=}C{=}CH{-}CHO$), 71276-86-3; MnL_3(*n*-$C_8H_{17}CH{=}C{=}CH{-}CH{=}CH{-}CO_2Me$), 71250-33-4; $CH_3C_5H_4Mn(CO)_3$, 12108-13-3; $CH_3C_5H_4Mn(CO)_2(THF)$, 51922-84-0

[1] *M. Franck-Neumann, D. Martina, F. Brion*, Angew. Chem. *90*, 736 (1978); Angew. Chem. Int. Ed. Engl. *17*, 690 (1978).

[2] Esters are cleaved almost quantitatively with iron(III) chloride, while in the case of ketones the use of cerium(IV) ammonium nitrate, which is more gentle, is necessary. Allenealdehydes can be isolated only when they are highly substituted: *M. Bertrand, G. Gil, J. Viala*, Tetrahedron Lett. *1979*, 1595; *J. C. Clinet, G. Linstrumelle*, Nouv. J. Chim. *1*, 373 (1977), and references cited therein.

[3] Direct acetylene-allene isomerization by bases is usually only of preparative importance in the case of electrophilic, homoconjugated derivatives; these are transformed into conjugated allenecarbonyl compounds. Even in this case the yields are often poor; see *R. J. Bushby*, Q. Rev. Chem. Soc. *24*, 585 (1970).

[4] The rate of isomerization strongly depends upon substituents E: thus, the isomerization at a weight to weight ratio of 1:50 (complex *(6)*: Al_2O_3) is complete in 15 min (E = CHO), 45 min (E = $COCH_3$) and 5—6 h (E = CO_2R).

[5] In the case of acetylene esters or ketones a 20% excess of $MeC_5H_4Mn(CO)_2(THF)$ is suitable, whereas in the case of acetylene aldehydes substoichiometric quantities of this reagent are necessary.

[6] *P. D. Landor, S. R. Landor, S. Mukasa*, Chem. Commun. *1971*, 1638.

[7] This compound was obtained by direct reaction of the ligand with $C_5H_5Mn(CO)_2(THF)$: *F. Edelmann, U. Behrens*, J. Organomet. Chem. *128*, 131 (1977).

[8] Pyrex glass apparatus; 15 °C; mercury high-pressure lamp (Philips HPK 125); under argon; *ca.* 2 h.

Ring-Opening of Lactones and Cyclic Carbonates with Bromo- or Iodotrimethylsilane

By *Hans R. Kricheldorf*[*]

It is known that iodotrimethylsilane is capable of cleaving acyclic, aliphatic esters[1,2], whereas bromotrimethylsilane fails to react. We have now found that the lactones *(1a—d)* and *(4)* undergo complete ring-opening on treatment with bromotrimethylsilane, while in the case of *(6)* only equilibrium with *ca.* 30% *(7)* is achieved. Iodotrimethylsilane also cleaves the lactones *(1a—d)*. The silyl esters of ω-bromo- and ω-iodocarboxylic acids *(2a—d)*, *(3a—d)*, and *(5)* are useful alkylating reagents, affording access to a wide range of compounds including ω-hydroxy-, ω-mercapto-, and ω-amino acid derivatives. Moreover, the esters of type *(2)*, *(3)*, and *(5)* can be converted with thionyl chloride directly into ω-halocarbonyl chlorides, *e.g.* *(8a—e)*. Of the numerous possible reactions of these acid chlorides we mention here the reaction with trimethylsilyl azide, which leads to the otherwise scarcely accessible ω-haloalkyl isocyanates *(9a—e)*. Table 1 lists the physical data of some of these compounds. The acid chlorides *(8a—c)* and the isocyanates *(9a—e)* are of interest not only for preparative organic chemistry but also for the synthesis and modification of polymers.

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$$\text{(1a-d)}\ \xrightarrow{BrSiMe_3} Br{-}(CH_2)_n{-}CO{-}OSiMe_3\ \text{(2a-d)}$$

$$\text{(1a-d)}\ \xrightarrow{ISiMe_3} I{-}(CH_2)_n{-}CO{-}OSiMe_3\ \text{(3a-d)}$$

n = 2-5

$$\text{(4)}\ \xrightarrow{+\,BrSiMe_3} Br{-}CH_2{-}CH_2{-}CH(Br){-}CO{-}OSiMe_3\ \text{(5)}$$

$$\text{(6)}\ \underset{-\,BrSiMe_3}{\overset{+\,BrSiMe_3}{\rightleftharpoons}}\ \text{(7)}$$

$$\text{(2a-d), (3d)} \longrightarrow X{-}(CH_2)_n{-}CO{-}Cl\ \text{(8a-e)}\ \xrightarrow[-\,N_2,\ -\,ClSiMe_3]{+\,N_3SiMe_3} X{-}(CH_2)_n{-}N{=}C{=}O\ \text{(9a-e)}$$

(a-d), X = Br, n = 2-5; *(e)*, X = I, n = 5

Table 1. Yield and physical data of ω-halocarboxylic acid derivatives, ω-bromoalkyl isocyanates, and ω-bromoalkoxysilanes.

Cpd.	Yield [%]	n_D^{20}	B.p. [°C/mbar]
(2a)	79	1.4453	75—76/12
(2b)	86	1.4489	87—89/11 45—47/0.1
(2c)	90	1.4522	54—56/0.03
(2d)	96	1.4541	75—77/0.07
(8a)	92	1.4939	49—51/12
(8b)	95	1.4896	70—71/12
(8c)	87	1.4913	43—45/0.2
(8d)	98	1.4877	60—62—0.3
(9a)	82	1.4838	44—46/12
(9b)	87	1.4840	65—66/12
(9c)	81	1.4842	84—86/12
(9d)	91	1.4861	56—58/0.1
(3a)	81	1.4799	39—41/0.2
(5)	84	1.4816	68—70/0.07
(11a)	84	1.4362	34—36/12
(11b)	79	1.4431	35—37/12

Cyclic carbonates can also be opened by bromotrimethylethylsilane, but the intermediary silyl carbonates immediately decarboxylate. In the case of *(10b)* ring-opening to *(11b)* is more than 95% regioselective. Since cyclic carbonates can readily be obtained from 1,2- and 1,3-diols, 1,2- and 1,3-disubstituted compounds containing two different reactive functions are accessible from them *via* this route. Iodotrimethylsilane reacts with cyclic and acyclic carbonates to give alkyl iodides. If ethylene carbonate is allowed to react with double the molar amount of iodotrimethylsilane in the cold, the initially formed carbonate *(12)* is attacked by the excess of $ISiMe_3$ before it decarboxylates; 1,2-diiodoethane is

formed as main product. This reaction course and the strongly exothermic reaction with lactones indicate that iodotrimethylsilane is considerably more reactive than bromotrimethylsilane.

$$\underset{(10a,\,b),\ R\,=\,H,\,CH_3}{R{-}\overset{|}{C}H{-}\overset{\backslash}{C}H_2,\ O{-}C({=}O){-}O\ \text{(ring)}} \xrightarrow[-CO_2]{+\,BrSiMe_3} \underset{(11a,\,b)}{R{-}\underset{|}{C}H{-}CH_2{-}Br,\ O{-}SiMe_3}$$

$$\downarrow +\,ISiMe_3$$

$$\underset{(12)}{I{-}CH_2CH_2O{-}CO{-}OSiMe_3} \xrightarrow[-CO_2]{+\,ISiMe_3} I{-}CH_2{-}CH_2{-}I + (Me_3Si)_2O$$

Sultones react neither with bromo- nor with iodotrimethylsilane, even though they are better alkylating reagents than lactones or carbonates. Since, however, the sulfonyl oxygen atoms are poorer nucleophiles than carbonyl oxygen atoms, we believe that the ring-opening of lactones and carbonates proceeds *via* a cyclic transition state *(13)*, in which the carbonyl oxygen is complexed by silicon *via* the vacant d-orbitals.

$$H_2C \cdots \ddot{O}{-}C({=}\ddot{O}\cdots Si);\quad X\cdots Si \qquad (13)$$

Procedure

Synthesis of trimethylsilyl 6-bromohexanoate *(2d)*: A mixture of 1 mol ε-caprolactone and 1.2 mol bromotrimethylsilane[3] is heated for *ca.* 10 h at 100 °C and *ca.* 30 h at 120 °C (or after addition of 20 ml CCl_4 heated under reflux for 30 h). *(2d)* is then isolated by distillation.—In the case of α-bromo-γ-butyrolactone *(4)* the reaction time must be prolonged; with β-propiolactone *(1a)* *ca.* 8 h suffices.

Synthesis of 6-bromohexanoyl chloride *(8d)*: A mixture of 1 mol *(2d)* and 1.1 mol distilled thionyl chloride in 250 ml anhydrous chloroform is heated to boiling until evolution of SO_2 ceases (*ca.* 4 h); *(8d)* is then isolated by distillation.—The reaction of *(8d)* with trimethylsilyl azide is carried out in chloroform or benzene[4].

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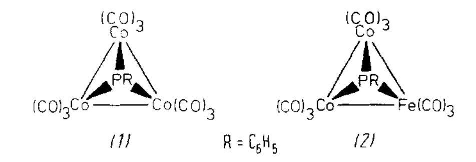
[1] *T.-L. Ho, G. Olah*, Angew. Chem. *88*, 847 (1976); Angew. Chem. Int. Ed. Engl. *15*, 774 (1976); cf. also *G. A. Olah, S. C. Narang, B. G. B. Gupta, R. Malhotra, ibid. 91*, 648 (1979) and *18*, 612 (1979), respectively.
[2] *M. E. Jung, M. Lyster*, J. Am. Chem. Soc. *99*, 968 (1977).
[3] *P. A. Mccuskey, E. L. Reilly*, J. Am. Chem. Soc. *75*, 1503 (1953).
[4] *H. R. Kricheldorf*, Synthesis *1972*, 551.

Experiments on the HOMO-LUMO Nature of Metal-Metal Bonds[**]

By *Harald Beurich, Thomas Madach, Felix Richter*, and *Heinrich Vahrenkamp*[*]

Dedicated to Professor Lawrence F. Dahl

The results of theoretical studies on metal-metal interactions range from the prediction of maximum bond energies[1] to the ascertainment of the absence of a direct bond[2]. Verification of such predictions is often just as difficult as the critical evaluation of the calculational procedures employed[3]. Experimental investigations are usually limited to isolated measurements on individual compounds[3]. Synthesis of the phosphorus-bridged trinuclear cluster *(2)*[4] has now made it possible to compare the results of *different* experimental methods for *(1)*[5] and *(2)*.



The cluster *(1)* contains one more electron than required by the 18-electron rule. On replacement of a cobalt atom by iron, however, all the metal atoms in *(2)* have closed electron shells. The nature of the excess unpaired electron in the HOMO of *(1)* becomes clear in a crystallographic comparison of *(1)* and *(2)*[6]: it is antibonding with respect to the metal-metal interaction. For, as in the corresponding complexes with sulfur atoms as bridging ligands[7], the metal-metal distances in *(2)* are shorter by *ca.* 10 pm than in *(1)* with essentially the same molecular geometry (cf. Fig. 1).

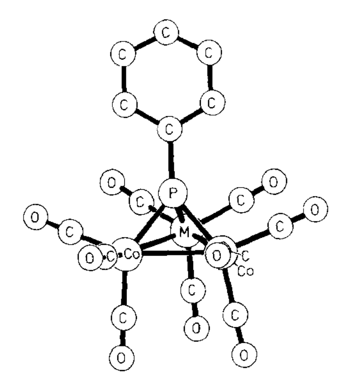


Fig. 1. Molecular structure of the clusters *(1)* (M = Co) and *(2)* (M = Fe). Principal bond lengths in *(1)*: Co Co = 271.2(3), 271.4(3), and 272.5(2); CO P = 212.3(4), 212.7(4), and 213.4(3); in *(2)*: Co Co = 263.2(2); Fe Co = 262.1(2) and 261.6(2); Co P = 212.0(2) and 212.2(2); Fe P = 216.2(3) pm.

This result is supplemented by the redox behavior of the two clusters. Only the oxidation of *(1)* to the monocation and the reduction of *(2)* to the monoanion can be observed as chemically and electrochemically reversible processes. Attempts at further oxidation led to destruction of the complexes. This means that occupation of the first antibonding orbital (*i. e.* the HOMO in *(1)* and the LUMO in *(2)*) does not effect decomposition but that this is brought about by an emptying of the highest bonding orbital (*i. e.* the HOMO in $(1)^{\oplus}$ and *(2)*). Since metal-metal single bonds number among the weakest bonds[3], it appears reasonable to assign essentially bonding metal-metal interactions to the HOMOs in $(1)^{\oplus}$ and *(2)*.

The ESR spectra (Fig. 2) supply further information about the first antibonding MOs of *(1)* and *(2)*. The 22-line pattern recorded for *(1)* demonstrates the interaction of the unpaired electron with all three cobalt atoms, and the 15-line pattern obtained for $(2)^{\ominus}$ reveals the corresponding interactions with the two cobalt atoms[8]. The good agreement of the HFS constants confirms the similarity of the two HOMOs. The most important result in both cases, however, is the absence of coupling with the phosphorus atom. The resolution of the ESR spectra is such that this coupling constant must be smaller than 1—2 gauss to escape detection. We have thus ob-

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